STUDY ON THE ADSORPTION PROPERTIES OF NOVEL CALIX[6]ARENE POLYMERS FOR HEAVY METAL CATIONS

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ABSTRACT

*A research has been conducted to investigate the capability of a series of novel calix[6]arenes-based polymers: poly-monoallyloxycalix[6]arene (**2a**), poly-monoallyloxypenta-estercalix[6]arene (**2b**) and poly-monoallyloxypenta-acidcalix[6]arene (**2c**) for trapping of heavy metal cations such as Cd(II), Cu(II) and Cr(III). The existence of active hydroxy group (-OH) and with a tunnel-like structure of the polymers, caused the polymers can be used as adsorbents for heavy metals. The adsorption process was carried out in batch method in the variation of acidity (pH), contact time and initial concentration of metal ions. The results showed that the amount of adsorbed metal increased with the increasing of the pH of metal solution. For these three polymers, the amount of metal ions Cd(II), Cu(II) and Cr(III) adsorbed was optimum at pH 7, 6 and 5 respectively. The optimum contact time for Cd(II) and Cu(II) was 120 min, while that for Cr(III) was 60 min. Study of the adsorption kinetics showed that the adsorption of Cd(II), Cu(II) and Cr(III) using polymer **2a** followed kinetics model of Ho. For adsorbent **2b** and **2c**, the adsorption kinetics of Cd(II) and Cr(III) also followed kinetics model of Ho while for the Cu(II) followed Lagergren kinetic models. Isothermal studies showed that the adsorption of metal ions on all adsorbents tend to follow the Langmuir isotherm. The adsorption energies of the three adsorbents were higher than 23 kJ/mole and polymer **2c** has the largest adsorption capacity for Cr(III).*

Keywords: *Calix[6]arene-based polymers; Cd(II); Cu(II); Cr(III); adsorption kinetic; isotherm adsorption*

ABSTRAK

*Telah dilakukan penelitian untuk mengkaji kemampuan adsorpsi senyawa turunan polikaliks[6]arena yaitu poli-monoalilkaliks[6]arena (**2a**), poli-monoalilesterkaliks[6]arena (**2b**) dan poli-monoalilasamkaliks[6]arena (**2c**) terhadap kation logam berat seperti Cd(II), Cu(II) dan Cr(III). Adanya gugus aktif hidroksi (-OH) dan struktur senyawa yang menyerupai terowongan sangat memungkinkan pemanfaatan senyawa-senyawa tersebut sebagai adsorben logam berat. Proses adsorpsi dilakukan dengan metode batch pada variasi keasaman (pH), waktu kontak dan konsentrasi awal ion logam. Hasil penelitian menunjukkan bahwa jumlah ion logam teradsorpsi semakin bertambah dengan bertambahnya pH larutan logam. Untuk ketiga polimer, jumlah ion logam Cd(II), Cu(II) dan Cr(III) masing-masing teradsorpsi optimum pada pH 7, 6 dan 5. Waktu kontak optimum untuk Cd(II) dan Cu(II) adalah 120 menit, sedangkan untuk Cr(III) adalah 60 menit. Kajian kinetika adsorpsi logam menunjukkan bahwa adsorpsi ion logam Cd(II), Cu(II) dan Cr(III) menggunakan polimer **2a** mengikuti model kinetika Ho. Sementara itu untuk adsorben **2b** dan **2c**, kinetika adsorpsi Cd(II) dan Cr(III) juga mengikuti model kinetika Ho sedangkan untuk Cu(II) mengikuti model kinetika Lagergren. Studi isotermal adsorpsi menunjukkan bahwa pola adsorpsi ion logam pada ketiga adsorben cenderung mengikuti pola isotermal Langmuir. Energi adsorpsi ketiga adsorben adalah lebih dari 23 kJ/mol dan polimer **2c** memiliki kapasitas adsorpsi terbesar untuk Cr(III).*

Kata Kunci: *poli-kaliks[6]arena; Cd(II); Cr(III); Cu(II); kinetika adsorpsi; isotermal adsorpsi*

INTRODUCTION

Heavy metals are major pollutants in various surface water or ground water in treated wastewater. It is great a concern because of the toxic effect of heavy metal ions to plants, animals and human beings [1-5]. Inorganic contaminants such as Cd(II), Cu(II) and Cr(III) are heavy metals which are difficult to be

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degraded into harmless species [6]. When these metals accumulate to reach toxic concentrations, it can certainly result in ecological damage.

The most commonly methods have been used to remove heavy metal ions from various aqueous solutions such as chemical precipitation, ion exchange, filtration and adsorption, etc. [7-8]. Among these methods, adsorption has increasingly received more attention in recent years because the method is simple, relatively low-cost and effective in removing heavy metal ions, especially at medium to low metal ion concentrations.

One of the potential compound to develop is calixarene. Calixarenes are such of macrocyclic compounds which have a fairly unique molecular geometry with almost unlimited derivate possibilities [9]. The peculiarity of the structure gives great potential for further development.

Calix[6]arene with six phenol ring arrange the molecules are relatively more easily made than calix[4]arene. It has provided important avenue to be used for various utilization. Several studies have shown that the calix[6]arenes and their derivatives widely used as an electrode to detect uranium (VI) in aqueous solution [10]. Furthermore its have been applied as catalysts in synthetic reactions [11] and in a number of instances, they were also used as a potential adsorbent for heavy metals, dye or organic wastewater [12-13].

To enhance the affinity of calixarenes toward metal ions, there are two general strategies have been adopted: either there have been incorporated different ionophoric groups including carbonyl, amide, nitrile and other suitable functionalities onto the calix-platform, or the calixarene units were fixed in a polymeric matrix. Various studies have been carried out in this regard, for instance, calix[6]-based polymers showed remarkable abilities to trap alkali metal ions and UO_2 [14]. The adsorption properties of calix[6]-amide polymers has been also reported toward soft cations (Ag^+, Hg^{2+}) and hard cations (Na^+, K^+) [15] and in our previous work, we have also synthesized poly-diallylcalix[6]arene and it has been investigated to trap Cr(III) cation [16].

Adsorption process is generally based on the interaction between metal and active groups existed on the surface of adsorbent through complex formation [17]. The hydroxy group on poly-calix[6]arene plays an important role as an active groups for cation binding. That phenolic OH groups can be substituted by other functional groups to produce derivatives that having different shapes and may act as effective and selective adsorbent.

Thus, continuation to our studies, herein we report the application of poly-monoallyloxy-calix[6]arene and their ester and acid derivatives as adsorbent for heavy metals. To research the adsorption capacity and mechanism of adsorbent, metal ion of Cd(II), Cu(II), and Cr(III) are chosen as adsorbate. Cd(II) metal ion representing of soft acid, Cu(II) metal ion representing of middle-class while the Cr metal ion represent the hard acid. Besides that the three metal ions are also the main pollutant in Indonesian waters.

EXPERIMENTAL SECTION

Materials

Poly-monoallyloxycalix[6]arene, poly-monoallyl oxypenta-estercalix[6]arene and poly-monoallyloxy penta-acidcalix[6]arene used in this study were prepared from *p-tert*-butylphenol according to the procedures reported previously [18], obtained according to synthetic method given in Fig. 1. The aqueous solution of Cd, Cu and Cr 1000 mg/L was prepared by using the analytical grade Merck product.

Instrumentation

Magnetic stirrer, concentration of the samples was analyzed by using Atomic Absorption Spectrophotometer (AAS, GBC Australia at Analytical Laboratory, UGM).

Procedure

The procedure of this research was carried out in the following stages, i.e. (1) adsorption studies for trapping of heavy metals, (2) adsorption kinetics, and (3) adsorption isotherm.

Adsorption Studies of Calix[6]arene Polymers for Trapping of Cd(II), Cu(II), and Cr(III)

Effect of pH. A series of 10 mL of each metal solution (Cd(II), Cu(II), and Cr(III)) 10 mg/L was prepared and the pH adjustments were performed with 0.1 M HCl or 0.1 M NaOH. Into every metal solution, 0.008 g of each polymer was poured and then stirred for 2 h. After filtering, the concentration of metal in the supernatant was analyzed by using atomic adsorption spectrometry (AAS).

Adsorption Kinetics. The kinetics experiments were investigated to determine the adsorption rate constant. Batch adsorption experiments were carried out by shaking 0.008 g of each polymer in 10 mL of the metal solution 10 mg/L at the optimum of pH for different reaction times (15–240 min). After filtering, the concentration of metal in the supernatant was analyzed by using AAS. The data was analyzed using three different adsorption kinetic models.

Adsorption Isotherm. Approach of either Langmuir and Freundlich isotherm models were also used to study

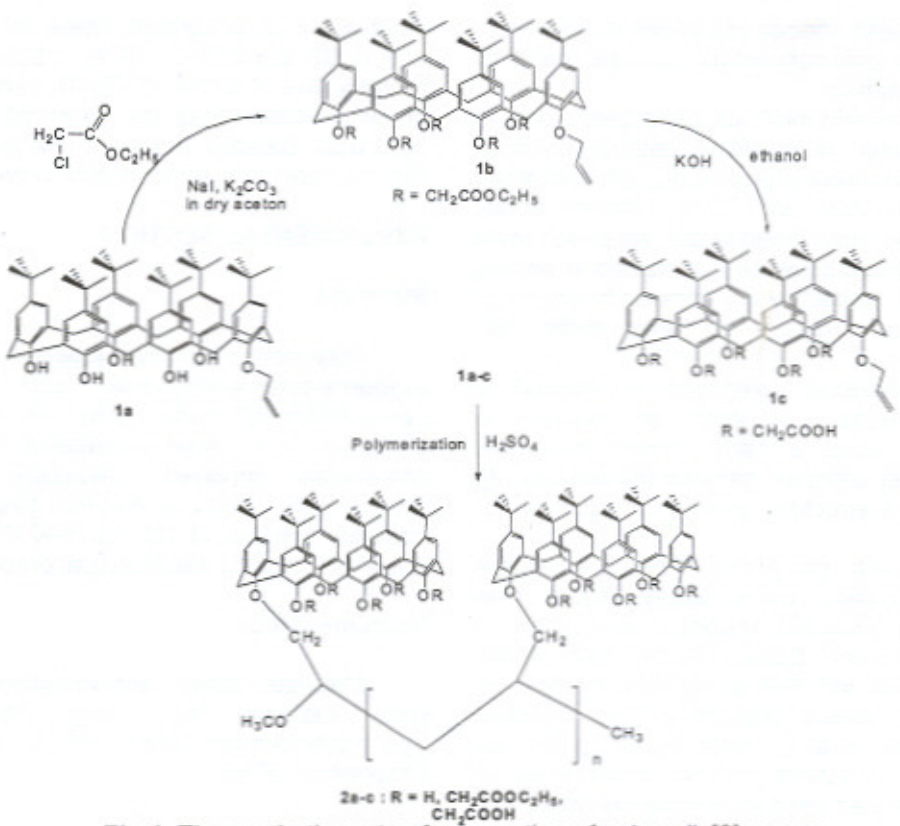

Fig 1. The synthetic route of preparation of poly-calix[6]arenes

the adsorption equilibrium of Cd(II), Cu(II), and Cr(III) by the polymers. As much as 0.008 g of each polymer was interacted with and stirred in 10 mL of solution containing the various concentrations of 4, 8, 12, 16, and 20 mg/L of each metal at the optimum of pH and contact time. After separating the supernatants, the concentration of metal in the supernatant was analyzed by AAS.

RESULT AND DISCUSSION

The synthesis of poly-calix[6]arene derived were prepared from *p-tert*-butylphenol which polymerized with concentrated sulfuric acid according to the procedures reported previously [18]. The scheme of the synthetic route of polymers was showed in Fig. 1.

The application of these polymers as adsorbent for Cd(II), Cu(II), and Cr(III) was investigated in batch systems. The adsorption parameters included the variation of pH, adsorption kinetic and adsorption isotherm.

Effect of pH

pH is one of the most important factors affecting the adsorption process. Adsorption ability of metal ions can depend on pH because of protonation of the anionic of Cd, Cu and Cr are in the form of Cd^{2+}, Cu^{2+}, and Cr^{3+}. Fig. 2-4 depicts the effect of pH on the adsorption of Cd(II), Cu(II), and Cr(III) ions on polycalix[6]arene.

It showed that the concentration of adsorbed metal increased with the increasing of the pH of metal solution. The increase of sorption from pH 2 to 5 must be caused by the decrease of the amount of H^+ in the medium, and therefore, the competition between metal ions and H^+ in occupying the active sites of the sorbents also decreased. For these three polymers, the concentration of metal ions Cd(II), Cr(III) and Cu(II) group [19]. Similarly, in poly-calix[6]arenes, the protonation of the phenolic-OH group is expected to play a role in the adsorption process.

In this study, the adsorption of Cd(II), Cu(II) and Cr(III) was studied at the pH range which the metal species optimum adsorbed at pH 7, 5 and 6 respectively. At pH value higher than 7, the sorption competed with the precipitation. A similar adsorption mechanism was presented by previous researchers on Cr(III) sorption onto poly-diallylcalix[6]arene [16] and on Cu(II) sorption onto calix[4]arene polymer [4].

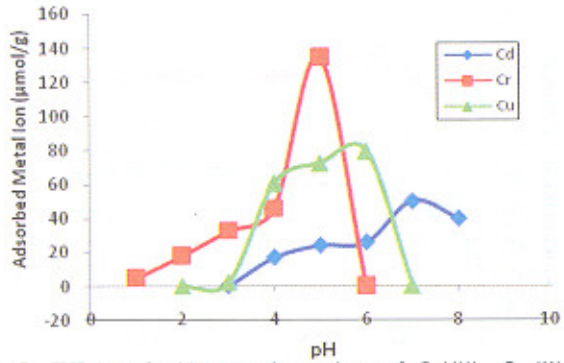

Fig 2. Effect of pH on adsorption of Cd(II), Cu(II) and Cr(III) onto polymer **2a**

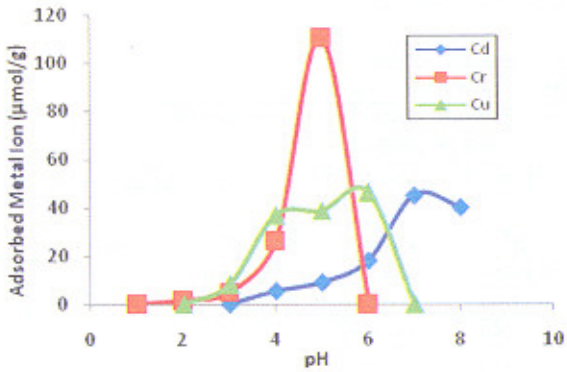

Fig 3. Effect of pH on adsorption of Cd(II), Cu(II) and Cr(III) onto polymer **2b**

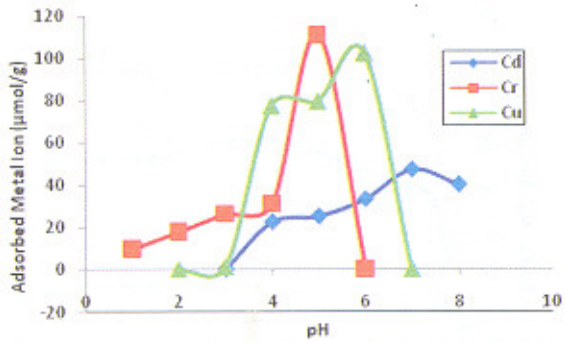

Fig 4. Effect of pH on adsorption of Cd(II), Cu(II) and Cr(III) onto polymer **2c**

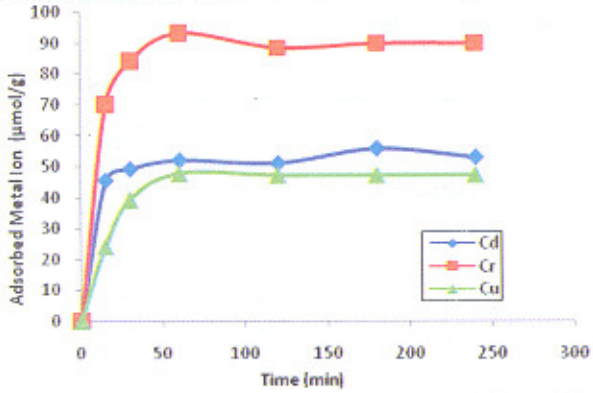

Fig 5. Effect of contact time on adsorption of metal ion onto polymer **2a**

Adsorption Kinetic Models

Adsorption metal process by calix[6]arene polymers conducted at constant temperature 25 °C. Fig. 5-7 presents the time dependence of the adsorption of metal ions. It was found that the adsorption of metal ions increased with increasing contact time and then having an equilibrium. For these three polymers, the optimum contact time for Cd(II) and Cu(II) is 120 min, while for Cr(III) is 60 min.

Parameter commonly used to study the rate of adsorption is the adsorption rate constant, k. From the data obtained, it can be analyzed to study the adsorption kinetics based on several models of the adsorption kinetics, i.e. a single ion of Santosa-Muzakky [20], pseudo first order (Lagergren), and the second order of the Ho [21].

Based on the data showed in Table 1, it shows that the kinetics model of Ho has a curve with a linearity higher than the kinetic model Santosa-Muzaky and Lagergren kinetic model for the third adsorption of metal ions using polymer **2a**. It can be concluded that all three metals adsorption using adsorbents **2a** tend to follow the pseudo second order. On the other hand, for adsorbent **2b** and **2c**, the adsorption kinetics of Cd(II) and Cr(III) followed kinetics model of Ho while for the Cu(II) followed Lagergren kinetic models. These results are similar by previous researchers [22] showed that adsorption of Cr(III) onto polypropylcalix[4]arenes followed the kinetics model of Ho. By using the three adsorbents, shows that the adsorption rate constant for Cr(III) is greatest when compared to the adsorption of Cd(II) and Cu(II). This means that within the same time, calix[6]arene polymers can adsorb Cr(III) more than Cd(II) and Cu(II).

Adsorption Isotherm

Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this study, both models were used to describe the relationship between the adsorbed amount of Cd(II), Cu(II), and Cr(III) and its equilibrium concentration in solution.

Langmuir isotherm model: $C/X_m = 1/bK + C/b$

Freundlich isotherm model: $\log X_m = \log B + 1/n (\log C)$

where:

C, the equilibrium concentration in solution

X_m, metal sorbed per g sorbent at equilibrium

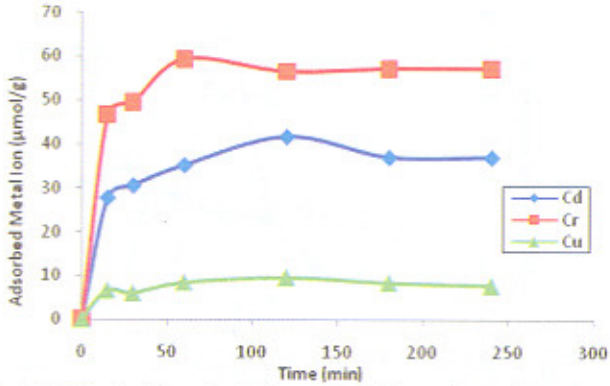

Fig 6. Effect of contact time on adsorption of metal ion onto polymer **2b**

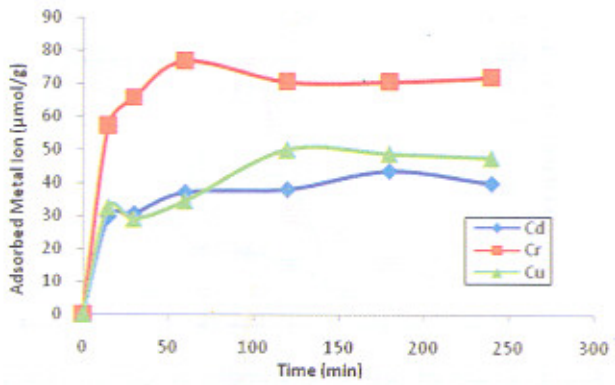

Fig 7. Effect of contact time on adsorption of metal ion onto polymer **2c**

Table 1. The Adsorption Kinetic Models

Equation		Adsorption Kinetic Models: Santosa-Muzakky $\ln\frac{Co}{Ca}/Co = K_1\frac{t}{Ca} + k$		Pseudo Orde 1 (Lagergren) $\ln(qe - qt) = \log qe - kt$		Pseudo Orde 2 (Ho) $\frac{t}{qt} = \frac{1}{2kqe^2} + \frac{1}{qe}$	
		R^2	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})
Adsorbent 2a	Cd	0,6366	1.2×10^{-3}	0,6658	2×10^{-5}	0,9098	4.5×10^{-7}
	Cu	0,4432	5×10^{-4}	0,7889	7.1×10^{-3}	0,8051	6.3×10^{-2}
	Cr	0,3151	5×10^{-4}	0,7926	3.2×10^{-3}	0,9203	1.03×10^{-2}
Adsorbent 2b	Cd	0.4500	9×10^{-4}	0.8001	2×10^{-3}	0.915	1.3×10^{-3}
	Cu	0.2418	4×10^{-5}	0.8671	1.1×10^{-3}	0.6798	10^{-2}
	Cr	0.4153	3×10^{-4}	0.8837	3.7×10^{-3}	0.9295	1.88×10^{-2}
Adsorbent 2c	Cd	0.7429	1.2×10^{-3}	0.8329	2.5×10^{-3}	0.9394	3.8×10^{-3}
	Cu	0.7000	6×10^{-4}	0.9511	3.5×10^{-3}	0.8761	1.15×10^{-2}
	Cr	0.2358	3×10^{-4}	0.8307	2.3×10^{-3}	0.9184	5.8×10^{-3}

Table 2. Langmuir and Freundlich Isotherm Models

Isotherm Parameters		Adsorbent 2a			Adsorbent 2b			Adsorbent 2c		
		Cd	Cu	Cr	Cd	Cu	Cr	Cd	Cu	Cr
Langmuir	Xm (µmol/g)	29.38	41.08	55.65	24.41	9.03	25.27	26.91	50.44	73.23
	$K \times 10^4$ (L/mol)	22.28	52.46	1.29	5.62	1.55	5.48	74.33	15.72	3.19
	ΔG (KJ/mol)	30.42	32.54	23.39	27.02	23.84	26.96	33.39	29.56	25.62
	R^2	0.9765	0.9583	0.8145	0.9767	0.8016	0.8840	0.9227	0.9117	0.8590
Freundlich	K (mol/g)	31.460	1.701	0.913	1.156	0.119	1.728	24.176	2.159	2.460
	R^2	0.1785	0.4876	0.8090	0.8754	0.6725	0.0129	0.2166	0.4845	0.2208

b, Langmuir's sorption capacity
K, sorption affinity
B, Freundlich's sorption capacity

The application of the two models are resulted the adsorption parameters as shown in Table 2. Table 2 showed that the linearity of the Langmuir isotherm model is higher than Freundlich isotherm model for all three metal ions. Thus the pattern of adsorption of Cd(II), Cr(III) and Cu(II) on the polymer **2a-c** tend to follow the Langmuir isotherm model. This means that the adsorption process occurs on the monolayer instead of multilayer. Therefore, it can be assumed that the maximum adsorption occurs when all of the active sites of adsorbents filled by the adsorbate forming the monolayer.

The adsorption capacity and energy can also be determined from the Langmuir equation. Adsorption energy equation can be written as $E_{ads} = -\Delta G^\circ = R\,T\,\ln K$, where R is an ideal gas constant (8.314 J K^{-1} $mole^{-1}$), T is temperature (Kelvin), and K is a the Langmuir constant (L/mole).

Table 3. Comparison of Metal Ion Adsorption on Calix[6]-Polymers and Other Adsorbents

Adsorbent	Metal	Xm (μmol/g)	Reference
Aminopropyl silica gel-calix[4]arene polymer (column methods)	Cu(II)	17.94	[4]
Poly-diallylcalix[6]arene (Batch methods)	Cr(III)	14.7	[16]
p-t-b-calix[4]arene (Batch methods)	Cu((II) Cr(III)	11.75 6.47	[24]
Poly-5-allyltetrahydroxy[4]arene (Batch methods)	Cr(III)	50.58	[25]
Baggase fly ash	Cu(II)	35.57	[26]
Grape stalks wastes	Cu(II)	47.21	[27]
poly-monoallyloxy-pentaacidcalix[6]arene (Batch methods)	Cu(II) Cr(III)	50.44 73.23	[current work]

The minimum energy of chemical adsorption is 5 kcal $mole^{-1}$ or 20 kJ $mole^{-1}$ [23]. Based on the data, the adsorption energies of the three adsorbents more than 23 kJ/mol. It means that the interactions between metal ions with the polymer **2a-c** can be viewed as a chemical adsorption process. This can be explained because the poly-calix[6]arenes have active sites such as hydroxy group (-OH), ester (-COOR) and carboxyl acid (-COOH) groups which can interact with Cu(II), Cd(II) and Cr(III). These active sites possess capability of capturing soft and hard metal ions. It can be understood that poly-calix[6]arene and their derivatives have electron donating of the OH groups or the O-containing carbonyl groups at their lower rim which can donate pair of electrons to the metal ion, forming coordination.

The results indicate that the maximum adsorption capacity of Cr(III) > Cu(II) > Cd(II). These phenomenon can be explained using the HSAB concept. Cu(II) is an acidic medium and Cd(II) is a soft acid because it has a large radius, while Cr(III) is a strong acid because it has a small radius and large charge. In the HSAB concept, soft acid will bind with soft bases, whereas hard acids will bind with hard bases. Active site on the adsorbent which is a strong base, so that it will be more stable binding to Cr(III) which is a strong acid as well. From these adsorption experimental results, it can be deduced that the adsorption capabilities were also influenced by the functional groups of calixarene polymers.

In general, the adsorption capacity of calix[6]-polymers i.e. polymers **2c** for Cu(II) and Cr(III) determined to be around 50.44 and 73.23μmol/g respectively, is higher than other materials. The value adsorption capacities in different adsorbents are summarized in Table 3.

The data show that the adsorption capacity of calix[6]arene polymers are relatively high when compared with other sorbent materials. Therefore, it can be said that calix[6]arene polymers can be regarded as a potential adsorbent for trapping of heavy metals.

CONCLUSION

The adsorption experiment towards series of cations showed that third polymers: poly-monoallyloxycalix[6]arene, poly-monoallyloxypenta-estercalix[6]arene and poly-monoallyloxypenta-acidcalix[6]arene can be selectively adsorbed for Cd(II), Cu(II), and Cr(III) cations. It has been observed that the amount of metal ions Cd(II), Cu(II)) and Cr(III) adsorbed was optimum at pH 7, 6 and 5 respectively. The adsorption of polymer **2a** fit the pseudo second order kinetic model. For adsorbent **2b** and **2c**, the adsorption kinetics of Cd(II) and Cr(III) also followed the pseudo second order kinetic model while for the Cu(II) followed the pseudo first order kinetic model. The adsorption behavior of Cd(II), Cu(II), and Cr(III) onto polymers **2a-c** obeys Langmuir's model. The adsorption energies of polymers **2a-c** more than 23 kJ/mol. It means that the interactions between metal ions with adsorbents can be viewed as a chemical adsorption process. It has been observed that polymer **2c** is more selective and efficient adsorbent for the removal of Cr(III). It was concluded that the functional groups of polymers play crucial roles in adsorption abilities. The adsorbents of calix[6]arene polymers can be regarded as a potential adsorbent in the application of heavy metals wastewater treatment.

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